Nanoscale Stability and Dissolution of Platinum Single Crystal Surfaces in Perchloric Acid Electrolyte

Scientific Achievement

One of the most critical issues in operation of a Proton Exchange Membrane Fuel Cell (PEMFC) is the gradual degradation of the active area of platinum catalysts. To understand the degradation mechanism, we investigated dissolution of Pt (111), Pt (100) and Pt (110) single crystal electrodes at three anodic potentials directly relevant to the operation of the low temperature PEMFC. Additionally we performed the similar experiment with the (111)-(100) nanofaceted platinum surface, which is an one-dimensional model of platinum nanoparticles.

For single crystal surfaces of Pt(111) and Pt(100), we find a considerable variation in dissolution rates depending on the surfaces and the potential at which the dissolution measurements were taken. More importantly, the rate does not increase monotonically, which offers a possibility that there is a potential window where the dissolution can be controlled. At 0.65 V vs. RHE all three basal Pt singe crystals dissolve considerably. Dissolution of Pt(111) occurs at the step edge, and proceeds by layer by layer. At 0.95 V vs. RHE, platinum content in solution is *smaller* than at 0.65V. Formation of atomic pits and deep (~3.5 nm, ~1 μm wide) holes in case of Pt(111), but step corrugation in Pt(100). At 1.15V vs. RHE, Pt(111) dissolves in "uncontrolled way" high content in solution (formation of many 0.6 nm deep rough etch holes). Pt(100) dissolves less that at two more negative potentials, surface looks almost unchanged. For Pt(111)-(100) nanofaceted surfaces, content of platinum in solution increases with the increased potential, at 1.15 V nanofacets dissolve almost completely within 24h loosing sharp features.

Significance

We performed the first atomic-scale measurements demonstrating the significance of atomic-level dissolution in the degradation of nanoparticle catalysts. Our measurements indicate that there is a potential window (~0.95 V) that all surfaces are strongly resistant to dissolution. We will continue similar measurements with nanoparticles. We will focus on the dissolution and shape evolution of the nanoparticles. We will also use electrochemical annealing using CO cycles to see if we can restore the surfaces. [V. Komanicky, X. Wang, A. Menzel, K. C. Chang, N. Markovic, D. Myers, H. You, ECS Transactions, Volume 1, (2006) in press]

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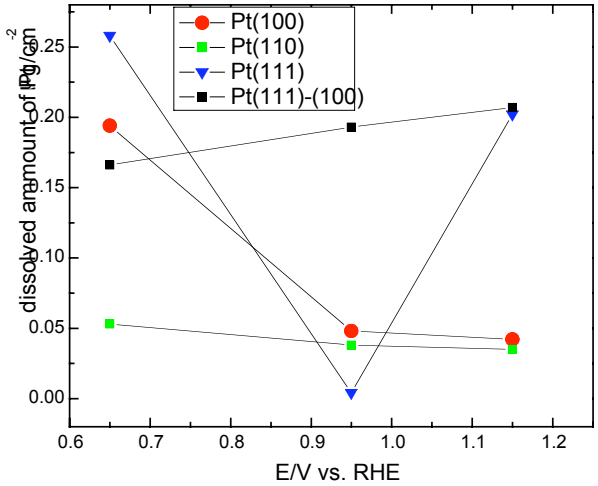
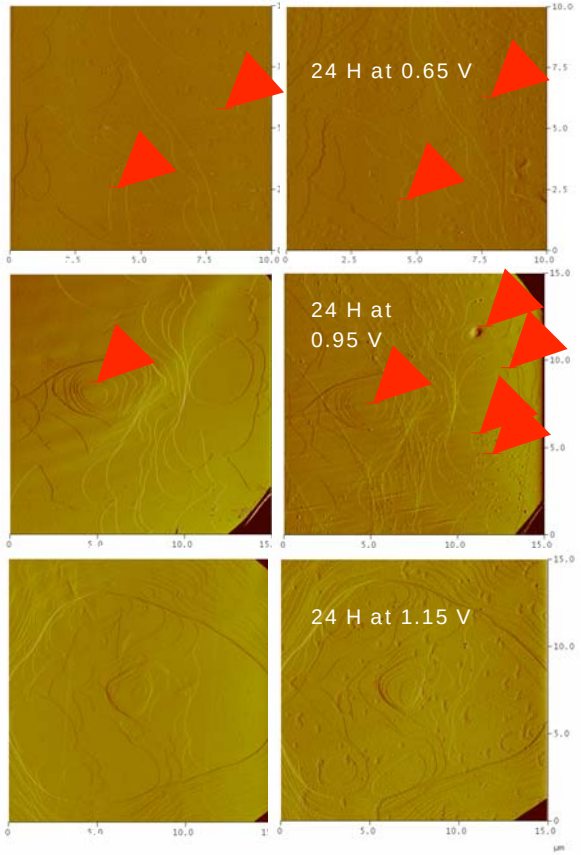
Pt dissolution rate is surface-specific and not monotonic to the holding potential



Before Dissolution

After Dissolution



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